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1. Title of the Invention

Production of Active Zinc White and Use Thereof

2. Scope of the Patent Claims

(1) Active zinc white characterized by having crystallite sizes of less than or equal to 500Å as measured by X-ray diffraction methods, and $10m^2/g$ or more of relative BET surface area and 0.05ml/g or more of porous volume.

(2) A manufacture method of active zinc white characterized by calcined breakdown of basic zinc carbonate at a temperature from 150°C to 500°C.

(3) An adsorption agent characterized by containing active zinc white having crystallite sizes of less than or equal to 500Å as measured by X-ray diffraction methods, and $10m^2/g$ or more of relative BET surface area and 0.05ml/g or more of porous volume as the effective ingredient.

3. Detailed Description of the Invention

Field of Industrial Use

This invention concerns active zinc white, its production and use, specifically it relates to the production method of active zinc white and the active zinc white which is activated to a high degree compared with zinc white exhibiting excellent absorbency of acidic gases and gases containing sulfur compounds.

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Conventional Technology

Heretofore, it is known that a variety of zinc compounds are use as adsorbents of foul smelling gases such as hydrogen sulfide.

For example, Japanese laid open patent specification Showa62-34565 describes how zinc compounds such as zinc chloride can be used as the effective ingredient in deodorants, moreover the said compounds can be added to porous supports such as zeolites to form deodorants. Moreover, in Japanese laid open patent specification Showa62-179463 a deodorant is described consisting of ionic zinc compounds such as zinc sulfate on a porous support.

Moreover, in Japanese laid open patent specification Showa62-152462 solid deodorization agents with basic zinc carbonate as the effective ingredient are described, in addition, in Japanese laid open patent specification Showa63-54935 a white deodorant consisting of an aggregate of micropowder of compacted zinc oxide, titanium dioxide and water is described.

Problem to be Solved by the Invention

The adsorption of hydrogen sulfide by zinc compounds is chemical adsorption by the formation of zinc sulfide, therefore it is to be expected that the adsorption efficiency would be higher the higher the zinc content of the zinc compounds used. Zinc oxide (zinc white) has the highest zinc content ratio of all zinc compounds, except for metallic zinc.

Heretofore, it is extremely surprising that of the zinc compounds suggested for deodorants and deodorizers zinc oxide was not included but this may be because the crystal particles of zinc white seen heretofore were very large, the relative BET surface area were small at 3 – 6m^2 /g as was the pore volume at 0.01cc/g, resulting in a low hydrogen sulfide adsorption volume of a few mg/g.

The inventors of the present invention discovered that by sintering basic zinc carbonate at a certain temperature the crystallites obtained are very small, the relative BET surface area and pore volume are very large, compared with conventional zinc white, and the adsorption speed and adsorption volume of sulfur compound containing gases, such as hydrogen sulfide, and acidic gases by the active zinc white is excellent.

However, the objective of the present invention is the provision of new activated zinc having small crystallite sizes as well as large relative surface area and pore volume and their manufacture method.

Another objective of the present invention is the provision of activated zinc having high adsorption speed and adsorption volume for gases containing sulfur compounds and acidic gases and a manufacture method thereof.

Yet another objective of the present invention is the provision of white adsorbents with high adsorption volume compared with conventional zinc deodorants and deodorizers.

Summary of the Invention

The present invention provides active zinc white characterized by having crystallite sizes of less than or equal to 500Å as measured by X-ray diffraction, and 10m^2/g or more of relative BET surface area and 0.05ml/g or more of porous volume.

Moreover, the active zinc white manufactured by the method of the present invention is characterized by calcined breakdown of basic zinc carbonate at a temperature from 150 °C to 500°C. In addition the present invention provides an adsorption agent characterized by containing as the effective ingredient active zinc white having crystallite sizes of less than or equal to 500Å as measured by X-ray diffraction, and $10m^2/g$ or more of relative BET surface area and 0.05ml/g or more of porous volume.

Effect

The zinc white of the present invention has a first characteristic of having crystallite sizes of less than or equal to 500Å as measured by X-ray diffraction, especially 50 to 300Å. The crystallite diameters are derived by the X-ray diffraction method using the Scherrer formula:

$$D = k\lambda/\beta \cos\theta \qquad \text{Formula (1)}$$

D: Crystallite size (Å)
k: Form factor (constant)
λ: Wavelength of the X-ray radiation used (Å)
β: Breadth of the diffraction which relates to the basic crystallite size (radians)
θ: Diffraction angle.

In Formula (1) D is the thickness in the direction perpendicular to the crystal surface D_{hkl}, in the case that half the breadth value of β is used as $\beta_{1/2}$, then the form factor constant k is 0.9. Where Cu Kα band radiation is used, then the biggest peak for zinc white is the (101) surface, $2\theta = 36.2°$, representing a face to alternate face of 2.479Å, in relation to this peak, if half the breadth value B_0 is measured then a correction factor may be obtained using the methods of Jorns et al, $\beta_{1/3} = \sqrt{(B_0^2 - b_0^2)}$ after measuring the standard substance (5 -10μm Si) under the same conditions.

In general, the zinc white available on the market has a crystallite breadth of 2000Å order, even what is called active zinc white is of the order of approximately 1000Å, whereas the active zinc white of the present invention has a crystallite breadth of 1/10 to 1/20 order of that.

Next, the second characteristic of the active zinc white of the present invention is that it has a BET relative surface area of $10m^2/g$ or more, specifically from 50 to $120m^2/g$ relative BET surface area, and a porous volume of 0.05ml/g or more, specifically 0.07 to 0.25ml/g. Moreover, compared to the conventional zinc white which has a relative BET surface area of one order of magnitude lower and a porous volume of only 0.01ml/g order, the BET relative surface area and porous volume values of the zinc white of the present invention are more than 10 times higher. Because the zinc white of the present invention has extremely high relative BET surface area and porous volume, the adsorption speed and adsorption volume for gases containing sulfur compounds and acidic gases are extremely high, also because the zinc content of zinc white is high (80.3weight%), with for example a test value of more than 30mg/g for flow breakdown of H_2S, especially 50mg/g and more, it can be seen that this is 30% of the theoretical adsorption volume. In contrast, for conventional zinc white the adsorption volume value does not exceed 1% of the theoretical value, thus this is a very surprising result.

The active zinc white of the present invention is manufactured by calcined breakdown of basic zinc carbonate at a temperature from 150°C to 500°C, preferably at 200°C to 400°C. It is critical that in this calcined breakdown the temperature is controlled to the above mentioned range to produce said active zinc white, if the temperature exceeds 500°C then the crystallite size exceeds the range of the present invention and the relative surface area and porous volume become less than the range of the present invention.

A representative formula of raw material usable as the basic zinc carbonate is:

$nZnCO_3 \cdot mZn(OH)_2 \cdot lH_2O$

[In the formula the n and m have values such that the formula n/m results in a number from 0.5 to 1] which becomes zinc white by decarboxylation and dehydration, but the zinc white crystallite sizes are controlled to be small by this specific temperature and the sites of decarboxylation and dehydration become active points and this is thought to lead to the increased relative surface area and porous volume.

Preferred Conditions of the Present Invention

Fig. 1 of the attached figures shows the X-ray diffraction patterns of conventional zinc white (A) and the active zinc white (B) of the present invention. From this Fig. 1, it can be seen that half the breadth value of the (101) surface of the active zinc white (B) of the present invention is increased greatly showing that the crystallite size has shrunk.

Fig. 2-A shows an electron microscope photograph of the structure of the particles of conventional zinc white (A), while Fig. 2-b shows an electron microscope photograph of the structure of the particles of the active zinc white (B) of the present invention, and Fig. 2-C shows the same kind of photograph of the particle structure of the basic zinc carbonate raw material. From these photographs it can be seen that, whereas the conventional zinc white (A) has a platy particle structure, the active zinc white (B) of the present invention retains the primary particle structure of the basic zinc carbonate raw material, and it is clear that it takes the structure of the secondary particulate structure with more apertures.

Even if the active zinc white of the present invention has an extraordinarily small crystallite size, the secondary particle size is relatively large and in the electron microscope photographs the secondary particle size is in the 0.1 - 5μm range, especially in the 1 - 3μm range, and in a Coulter Counter the median diameter D_{50} was 0.5μm to 5μm , more specifically in the 1 - 3μm range.

The attached Figs. 3-A and 3-B show pore diameter distribution of the conventional zinc white (A) and active zinc white (B) as measured by the BET method. In contrast to the conventional zinc white which has almost no pores, the active zinc white (B) of the present invention clearly has a sharp peak in the distribution at pore diameter 10 to 60Å. The active zinc of the present invention has an average pore diameter of 20 to 40Å.

The calcined breakdown of basic zinc carbonate can be carried out at atmospheric pressure in air, but depending on preferences may be carried out in oxidative atmospheres, in inactive gases such as nitrogen or in reductive atmospheres. The sintering may be carried out in vacuum or at reduced pressures of 0.1 to 200mmHg (Absolute). The calcined breakdown may be carried out in a muffle oven, electric oven, rotary kiln or in a

flow style calcining oven. The active zinc white produced by calcined breakdown should always be powdered and graded.

The active zinc white of the present invention may be utilized as a deodorant, deodorizer or as an adsorbent for other purposes.

This adsorbent may be in the form of a powder, granule, pellet, tablet or formed into any shape to provide the adsorbent agent for use. This adsorbent is white in color and because the constituent substance is highly stable, it is non-polluting and may be filled in to every type of adsorbent holder as a powder or in a paper or fabric bag, a filter holder, a cartridge type container. Of course, if used as a granulate, then its handling is that much more simplified.

In forming granules every kind of inorganic binder such as sticky clay, water glass, bentonite and hectorite, or organic binders such as any kind of synthetic resin such as polyvinylalcohol, carboxymethlycellulose, or latex type synthetic rubber can be used, and the zinc white content of particulates should be 50 to 95%, preferably 70 to 90%, moreover the dimensions should be generally 0.1mm to 5mm, more especially 0.5 to 3mm range is preferred.

Of course the adsorbents of the present invention may be mixed with one or more of said active zinc white, activated carbon, silica gel, alumina gel, silica-alumina gel, magnesium silicate, zinc silicate, calcium silicate, titanium hydroxide gel, zinc titanate, zirconium hydroxide, activated clay, silica phosphate, titanium phosphate or zeolite and when so mixed the ratio of active zinc white to other adsorbents can be 5:95 to 80:20, more preferably 10:90 to 70:30 on a weight ratio basis.

The adsorbents of the present invention exhibit superior adsorption speed and adsorption volume for sulfur containing gases such as hydrogen sulfide, all kinds of mercaptans, SO_x, as well as acidic gases such as carbon dioxide, NO_x, halogen gases, halogenated hydrogen gases, cyanide, organic acids, and the like.

Effect of the Invention

The active zinc white provided by the present invention has very small crystallite size and a large relative BET surface area and pore volume, and because the active zinc white has the said characteristics and a high zinc content, it exhibits excellent adsorption speed and adsorption volume for gases containing sulfur compounds and acidic gases.

Examples

The present invention is explained using the following examples.

The measurement methods of every matter in this specification are detailed as follows.

Measurement Methods

(1) Crystallite

A Rigaku Denki (K.K.) X-ray diffraction device (X-ray generating device CN4036A2, goniometerCN255D5, computation device CN2726A1) was used and measurements made under conditions described below and processed in an automatic analysis program to measure the crystallites.

Voltage	40KVP
Current	20mA

Count Full scale	8000C/S
Irradiation Angle	1°
Slit Width	0.15mm

The recording operation was carried out at a step scan of 0.02°.

(2) Relative BET Surface Area

An automatic BET (relative surface area) measurement device (Sorptomatic Series 1800 manufactured by CARLO-ERBA) was used to measure BET.

(3) Porous Volume and Pore Distribution

The adsorption isotherms measured by the automatic BET (relative surface area) measurement device (Sorptomatic Series 1800 manufactured by CARLO-ERBA) were used in a Cranston-Inkly method computation program to complete the measurement.

(4) Adsorption Volume of Hydrogen Sulfide and Ethylmercaptan

A specific amount of gas was presented from a gas reserve 5 and liquid injected by syringe using the devices shown in Fig 4. The adsorption test substance was forced in from vessel 8 using tank 6 and the flow adjusted to 200ml/min using flowmeter 7. At arbitrary intervals a set volume of gas was sampled and the remaining concentration was measured in a gas chromatography (FPD). If there was no breakthrough with a specific volume of gas, the same process was repeated to derive the adsorption volume index.

Example 1

140g of zinc chloride (Premium Lab Grade) was placed in a 2 liter glass beaker and water was added to dissolve and the volume brought up to 1.5liters (Solution A). 110g of sodium carbonate (Premium Lab Grade) were added to another 2 liter glass beaker and water was added to dissolve and the volume brought up to 1.5liters (Solution B). With solution A as the mother solution stirred at 40°C then solution B was poured in at a speed of 20ml/minute. When all was poured in the pH of the reaction solution was 7.8. The reaction solution was suction filtered, washed with water and dried at 110°C. The cake obtained was pulverized in an impact powder mill (sample mill) to obtain a fine white powder (Process 1).

When the powder obtained from Process 1 was subjected to X-ray analysis it was determined to be basic zinc carbonate with a relative BET surface volume of 25.6m^2/g.

50g of the basic zinc carbonate obtained in process 1 was placed in a porcelain evaporator dish to a thickness of about 1cm and was calcined at 300°C in an electric muffle oven for 3 hours. When the powder derived was analyzed by X-rays it was found to be zinc oxide (Process 2).

Example 2

Basic zinc carbonate was prepared by the same process as in Example 1 process 1 but calcined at 400°C to yield zinc oxide.

Example 3

Basic zinc carbonate was prepared by the same process as in Example 1 process 1 but calcined at 500°C to yield zinc oxide.

Example 4

Basic zinc carbonate was prepared by the same process as in Example 1 process 1 but calcined at 200°C for 20 hours to yield zinc oxide.

Example 5

50g of commercially available industrial zinc carbonate (made by Nihon Kagaku Sangyo) and subjected to the same processes as in Example 1 and calcined at 300° to yield zinc oxide.

Example 6

30g of basic zinc carbonate obtained by process 1 of Example 1 was placed in a glass reaction vessel and calcined at 300°C in an electric muffle oven under reduced pressure (1mmHg) for 3 hours to yield zinc oxide.

Comparative Examples 1 – 2

In Comparative example 1 premium lab grade zinc oxide (Manufactured by Junsei Kagaku), and in Comparative Example 2 industrial use basic zinc carbonate (Manufactured by Nihon Kagaku Sangyo) were used.

Comparative Example 3

Basic zinc carbonate was prepared by the same process as in Example 1 process 1 but calcined at 700°C to yield zinc oxide.

Comparative Example 4

Commercially available industrial use basic zinc carbonate (Manufactured by Nihon Kagaku Sangyo) was treated as in Example 1 and calcined at 700°C to obtain zinc oxide.

The results of measurement of relative BET surface area, hydrogen sulfide adsorption volume and ethylmercaptan adsorption volume of the zinc oxide crystallites obtained in Examples 1-6 and Comparative Examples 1-4 are shown in Table 1.

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[Table. 1]

	Crystallite (Å)	Relative BET Surface Area (m^2/g)	BET Porous Volume (cc/g)	Adsorption Volume of Hydrogen Sulfide (mg/g)	Adsorption Volume of Ethly Mercaptan (ml/g)
Example 1	102	98.3	0.188	124.9	10.8
Example 2	149	79.5	0.113	84.8	8.9
Example 3	201	55.2	0.062	59.6	6.3
Example 4	98	106.2	0.201	120.4	10.1
Example 5	107	87.5	0.179	118.7	9.4
Example 6	104	105.4	0.213	74.8	9.7
Comparative Example 1	2487	1.1	0.013	6.0	1.8
Comparative Example 2	-	16.4	0.052	54.5	1.0
Comparative Example 3	710	9.6	0.029	11.8	2.4
Comparative Example 4	1083	5.2	0.020	9.1	1.9

4.Brief Description of the Drawings

Fig 1(A) is the X-ray diffraction spectrum using Cu – Kα band radiation on conventional zinc white, while (B) is that of active zinc white produced in Example 1 of the present invention.

Fig. 2-A is the electron microscope photograph showing the particle structure of conventional zinc white of Comparative Example 1, Fig. 2-B is that of basic zinc carbonate of Comparative Example 2, while Fig. 2-C is that of the active zinc white of Example 1 of the present invention.

Fig. 3-A is a pore size distribution graph obtained using the BET Method (Cranston-Inkly Method) on the conventional zinc white of Comparative Example 1, while Fig. 3-B shows that of the active zinc white of the present invention.

Fig. 4 is an abbreviated outline drawing of the adsorption volume measurement device.

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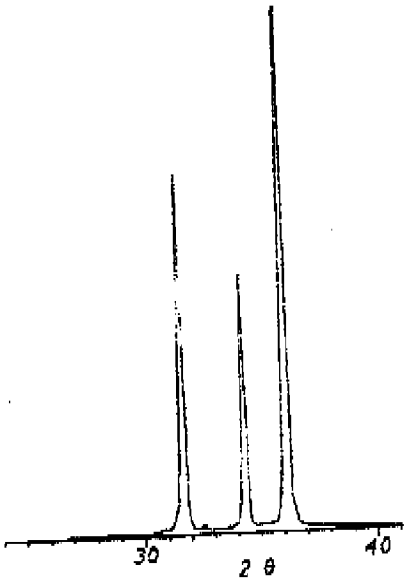
[Fig. 1]

(A)



(B)

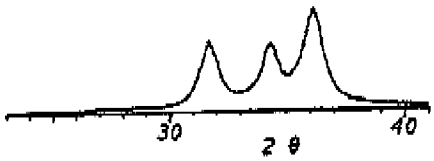


Fig. 2-A

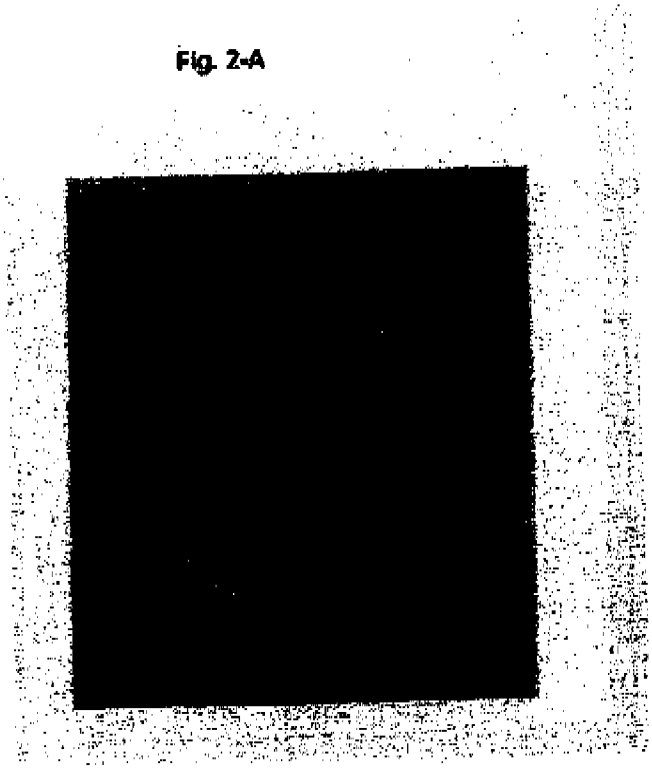


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Fig. 2-B

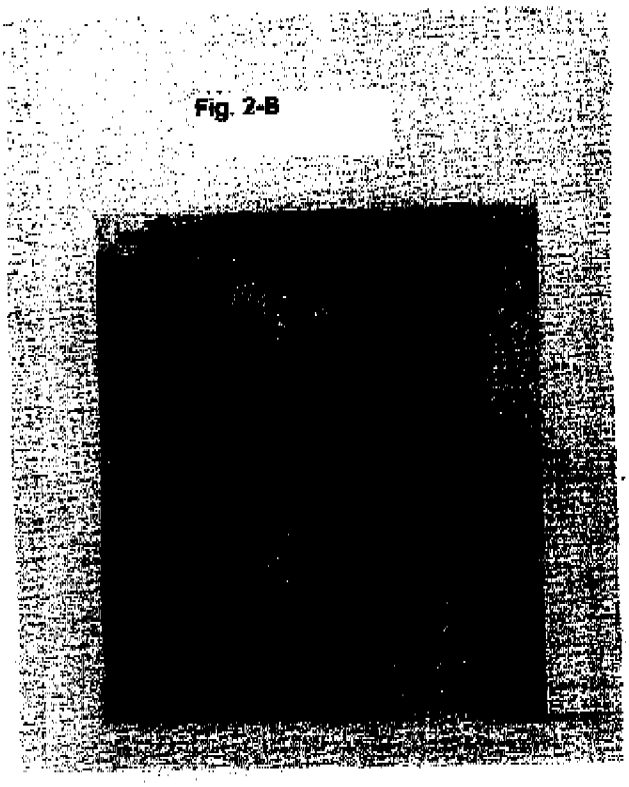
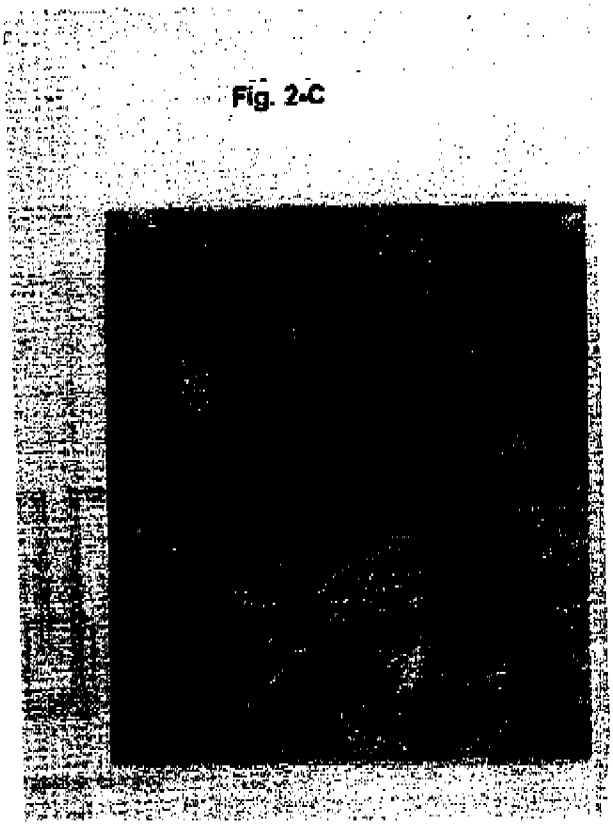


Fig. 2-C



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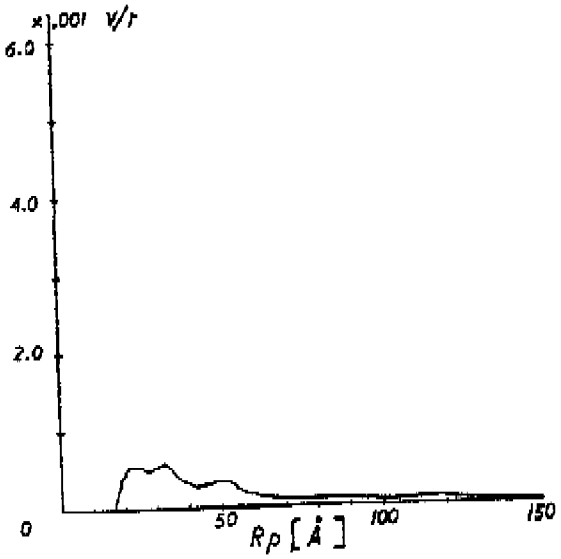
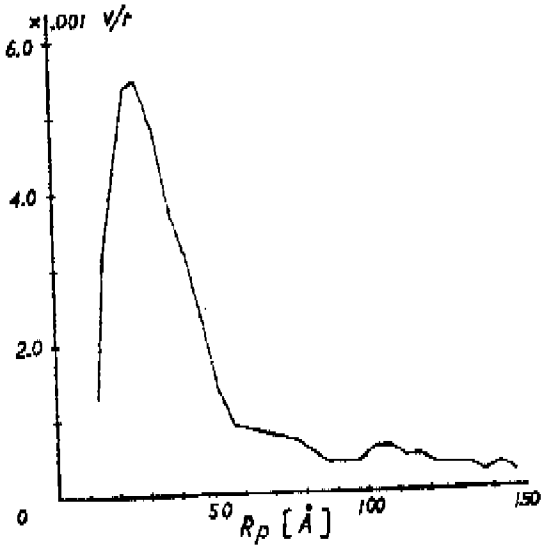
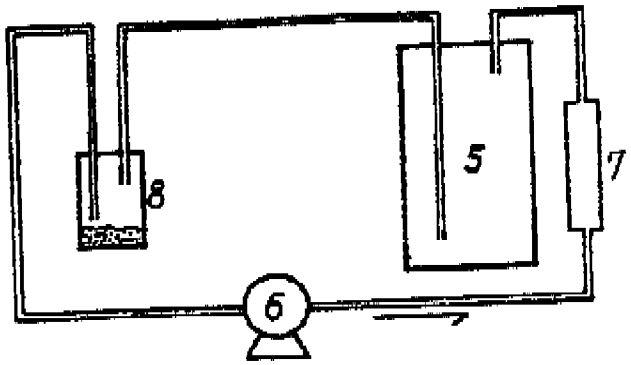
[Fig. 3-A]



[Fig. 3-B]



[Fig. 4]